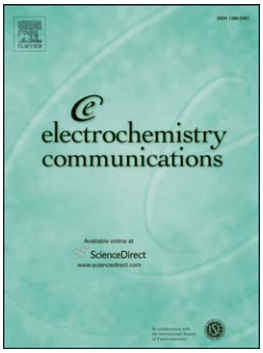

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Oxygen reduction reaction on carbon-supported palladium nanocubes in alkaline media

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Abstract

Carbon-supported Pd nanocubes with the size of 30, 10 and 7 nm were prepared and their electrocatalytic activity towards the oxygen reduction reaction (ORR) in alkaline solution was studied. For comparison carbon-supported spherical Pd nanoparticles and commercial Pd/C catalyst were used. The catalysts were characterised by transmission electron microscopy, electro-oxidation of carbon monoxide and cyclic voltammetry and the ORR activity was evaluated using the rotating disk electrode method. The ORR on all studied Pd/C catalysts proceeded via four-electron pathway where the rate-limiting step was the transfer of the first electron to O_2 molecule. The specific activity of Pd nanocubes was more than two times higher than that of spherical Pd nanoparticles and increased with increasing the particle size.

Keywords: Oxygen reduction, Pd nanocubes, Supported catalysts, Electrocatalysis

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1. Introduction

Platinum is the best electrocatalyst among pure metals for oxygen reduction reaction (ORR) and palladium has proven to be suitable substitution for it as both metals are in the same group in the periodic table, have same crystal structure, similar atomic size and the ORR proceeds via same reaction mechanism [1, 2]. Jiang et al. found that on Pd catalysts the ORR in alkaline solution exhibits particle size effect as the specific activity increases continuously by a factor of three with increasing particle size from 3 to 16.7 nm, while the mass activity showed a maximum at Pd particle size of 5 nm [3]. It was suggested that the increased adsorption of OH^- decreases the number of active sites for ORR, thus decreasing the specific activity. The mass activities increased with decreasing particle size as larger number of Pd atoms participated in the surface catalysed reactions and in combination of specific activity the optimum Pd particle size was suggested to be around 5 nm. The same workgroup has also reported that in alkaline media Pd nanoparticles (PdNPs) have higher activity towards the ORR than Pt nanoparticles (PtNPs), which was explained by the differences in surface oxidation [4]. Similar results were reported for graphene-supported PdNPs and PtNPs [5].

On both Pd and Pt the electroreduction of oxygen is a structure-sensitive reaction [2]. Kondo et al. showed that in perchloric acid solution the activity of Pd single-crystal facets rises in the following order: Pd(110)<Pd(111)<Pd(100) [6]. In addition, it has been shown that oxide film is not relevant to the ORR on n(111)-(100) series of Pd at 0.9 V vs RHE in perchloric acid and (111) terrace is the active site for ORR [7]. Cai et al. treated particles in Br^--containing solution to reduce surface roughness and to increase Pd(111) surface sites, as a result a significant improvement in specific activity and mass activity was observed as compared to untreated particles [8]. The reduction of oxygen on unsupported Pd nanocubes has been studied in both acidic and alkaline solutions and enhanced ORR activity of cubic PdNPs has been demonstrated, which has been suggested to arise from the Pd(100) single-crystal facet

[9-14]. Shao et al. showed that carbon-supported Pd nanocubes in acidic solution exhibit 10 times higher specific activity than octahedral Pd nanoparticles which have predominantly Pd(111) facets on the surface [15]. Liu and co-workers tested 27, 48 and 63 nm Pd cubes for ORR and from these 48 nm nanocubes were found to be the most active. The activity surpassed that of 9 nm spherical Pd nanoparticles and was suggested to be due to decreased OH^- adsorption [11]. However, Huang et al. showed that the kinetic current density of the ORR on Pd nanocubes was rather similar in 0.1 M and 1 M NaOH solutions [14]. Recently, Liu et al. demonstrated the influence of supporting material of Pd nanocubes on the ORR in alkaline solution [16]. It was found that the reduced graphene oxide nanosheets improve the ORR onset potential of the catalyst.

In this study three different size carbon-supported Pd nanocubes were prepared and their activity towards the ORR in alkaline solution was tested to find out if changing the particle size or metal loading on carbon has an effect on the electrocatalytic activity of the catalysts. In acid media the carbon-supported Pd nanocubes had higher specific activity than spherical Pd nanoparticles and commercial Pd/C catalyst [17] and therefore the purpose of the present research was to compare the ORR activity trends in 0.1 M KOH.

2. Experimental

Pd nanocubes were prepared by methods described previously using ascorbic acid as reducing agent and cetyltrimethylammonium bromide or polyvinylpyrrolidone as capping agent [18-20]. After the synthesis, Vulcan XC72 carbon was added to form 20 wt% and 50 wt% Pd/C catalyst. The samples were cleaned by adding NaOH pellets to the suspension, filtered and washed several times with water [21]. Finally the catalysts were dried overnight at 75 °C. The catalysts are designated as PdCub1-20, PdCub1-50, PdCub2-20 and PdCub3-20, where PdCub1, PdCub2 and PdCub3 correspond to Pd nanoparticle size of 30, 10 and 7 nm,

respectively and 20 or 50 indicate Pd loading on carbon. For comparison purposes, carbon-supported spherical Pd nanoparticles were prepared (PdSph-20) [9, 22] and commercial Pd/C catalyst (20 wt% Premetek Co, USA) was also tested.

The catalyst ink (1 mg ml^{-1}) was prepared by mixing the catalyst powder in water containing 0.5% of Nafion (Aldrich) and pipetted onto the glassy carbon (GC) electrode (5 mm in diam.) to have the Pd/C catalyst loading of 0.1 mg cm^{-2}. The electrochemical measurements were carried out in 0.1 M KOH solution, which was saturated with Ar (99.999%, AGA) or O_2 (99.999%, AGA). The solution was made from KOH pellets (puriss p.a., Sigma-Aldrich) and Milli-Q water. The electrochemical measurements were carried out in three-electrode glass cell with reversible hydrogen electrode (RHE) as reference (all potentials are given with respect to RHE) and a Pt wire separated by a glass frit served as a counter electrode. An EDI101 rotator with CTV101 speed control unit (Radiometer) was used for rotating disk electrode (RDE) experiments. The potential was applied with Autolab PGSTAT30 potentiostat/galvanostat (Metrohm Autolab). The experiments of CO stripping, cyclic voltammetry (CV) and oxygen reduction were carried out similarly to previous publications [9, 10, 17]. The experiments were repeated five times for better evaluation of the catalysts.

For transmission electron microscopy (TEM) images JEM-2010 (JEOL) instrument was used.

The thermogravimetric analysis (TGA) was carried out using a Mettler-Toledo TGA/SDTA851 thermobalance with a temperature ramp of 10 ºC min^{-1} from 25 to 850 ºC in an oxidative atmosphere (N_2:O_2 = 4:1).

3. Results and discussion

3.1. Physical characterisation of Pd/C catalysts

The representative TEM images of carbon-supported Pd nanocubes are presented in Figure 1. As expected, the majority of the particles are cubic and the particle size depends on the

synthesis method employed, being about 30 nm for PdCub1, 10 nm for PdCub2 and 7 nm for PdCub3. Based on previous studies it is safe to assume that the Pd(100) crystal facet prevails on the surface of these nanocubes [10, 22].

The real Pd content in the catalysts determined by thermogravimetric analysis was in good agreement with the expected values: PdCub1-20 contained 18 wt%, PdCub1-50 49 wt%, PdCub2-20 18 wt% and PdCub3-20 19 wt% of Pd.

3.2. CO stripping and CV studies

First the studied electrodes were subjected to oxidation of pre-adsorbed CO, in order to clean and characterise the surface. Figure 2a shows that initially the whole surface is blocked with CO, which is oxidised completely during one potential cycle up to 1 V, resulting an oxidation peak at ca. 0.8 V. After the CO stripping experiments potential was cycled between 0.1 and 0.8 V for additional cleaning and characterisation. After the ORR measurements the CV curves were registered between 0.1 and 1.4 V (Figure 2b) in order to calculate the electroactive surface area of Pd using the value of 424 μC cm^{-2} as charge density associated with the reduction of a monolayer of PdO [23]. It is important to avoid the destruction of the nanocubes prior to the oxygen reduction studies as they lose their shape on prolonged potential cycling between 0 and 0.9 V vs RHE [24]. The general features of CVs for all the studied Pd/C catalysts were similar, current started to increase at about 0.7 V on positive going scan as surface is oxidised and the reduction of these oxides caused well-defined cathodic peak at 0.7 V. An additional current increase from 0.3 V is related to the adsorption of hydrogen, which is desorbed in reverse scan. In alkaline solution the characteristic peaks for hydrogen adsorption/desorption are not well-defined [10].

3.3. Oxygen reduction in alkaline solution

After CO oxidation and CV studies the electrodes were transferred to another electrochemical cell in which 0.1 M KOH solution was saturated with oxygen. The RDE results of PdCub3-20 are presented in Figure 3a. With all Pd catalysts single-wave polarisation curves with well-defined current plateaus were obtained (Figure 3c). The plateau current densities are lower than that observed on bulk Pd in alkaline solution [10], which is the effect of Nafion, as it has been shown to reduce limiting current density [25]. Small differences in plateau currents are apparently due to uneven thickness of catalyst layer on the electrodes as well as variations in geometrical electrode area coated with the catalyst. The half-wave potential slightly decreased in the following order: PdCub1-50 > PdCub3-20 > PdCub2-20 ≈ PdSph-20 ≈ commercial Pd/C > PdCub1-20 showing enhanced ORR activity of the smallest Pd nanocubes as compared to spherical PdNPs. The Koutecky-Levich (K-L) equation was used to analyse the RDE data:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} + \frac{1}{j_f} = \frac{1}{j_k} + \frac{1}{0.62nFD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}^{b}\omega^{1/2}} + \frac{1}{j_f} \qquad (1)$$

where j is the measured current density, j_k is the kinetic current density, j_d is the diffusion-limited current density, j_f is the limiting diffusion current density in Nafion, n is the number of electrons transferred per O_2 molecule, F is Faraday constant (96485 C mol^{-1}), ω is the electrode rotation rate (rad s^{-1}), $C_{O_2}^{b}$ is the concentration of oxygen in the bulk (1.2×10^{-6} mol cm^{-3}) [26], D_{O_2} is the diffusion coefficient of oxygen (1.9×10^{-5} cm^2 s^{-1}) [26] and ν is the kinematic viscosity of the solution (0.01 cm^2 s^{-1}) [27]. From the slope of K-L lines the n value was found (Figure 3b). For all Pd/C catalysts the value of n was close to 4, showing that the main product of the ORR is water. This finding coincides with the previous studies conducted on Pd-based catalysts where the 4-electron pathway of the ORR prevails [3, 10, 28-30].

In order to compare the activity of Pd nanoparticles, the specific activities (SA) and mass-activities (MA) of the catalysts were calculated:

$SA = I_k / A_r$ (2)

$MA = I_k / m_{Pd}$ (3)

where I_k is kinetic current at a given potential, A_r is the electroactive surface area and m_{Pd} is the mass of Pd on the electrode. The SA values at 0.9 V increased in the following order: PdSph-20 (0.15 ± 0.08 mA cm^{-2}) < commercial Pd/C (0.21 ± 0.09 mA cm^{-2}) < PdCub3-20 (0.37 ± 0.10 mA cm^{-2}) < PdCub2-20 (0.42 ± 0.05 mA cm^{-2}) < PdCub1-50 (0.50 ± 0.08 mA cm^{-2}) < PdCub1-20 (0.55 ± 0.08 mA cm^{-2}). In perchloric acid solution it has been determined that Pd(100) is the most active single-crystal facet for Pd [6]. While there have not been systematic studies on Pd(hkl) in alkaline solution, the same tendency is expected based on the ORR results of Pd nanocubes where it was shown that cubic PdNPs have more than two times higher SA value than that of bulk Pd and spherical PdNPs [10]. Thus, the smaller SA for PdCub2-20 and PdCub3-20 could be explained by the fact that truncation of the smaller particles decreases the relative surface area of Pd(100) facet as compared to larger particles. The SA value for PdSph-20 was more than two times lower than those of Pd nanocubes, which is in good agreement with our previous study on unsupported Pd nanocubes [10]. In contrast Shao et al. did not find any structural dependence of Pd nanocubes, octahedra and conventional Pd nanoparticles in alkaline solution [31]. It has been demonstrated that the SA increases with increasing the Pd particle size [3]. By taking these observations into account we can assume that the increase in SA could be attributed to the increase of the particle size and the relative amount of Pd(100) crystal facet.

For practical applications high SA is not sufficient, the mass-activities should also be high. The MA values at 0.9 V decreased in the order of PdSph-20 (101 ± 13 A g^{-1}) > PdCub3-20 (87 ± 16 A g^{-1}) ≈ commercial Pd/C (87 ± 12 A g^{-1}) > PdCub2-20 (62 ± 11 A g^{-1}) > PdCub1-20 (59 ± 12 A g^{-1}) > PdCub1-50 (38 ± 9 A g^{-1}), following the sequence of increasing the particle size. In a previous study Jiang et al. showed that MA for Pd/C has a maximum at about 5 nm

particle size [3], thus these results suggest that further decreasing the size of Pd nanocubes should yield a catalyst with higher SA and MA than PdSph-20 used in this study, but the MA of the commercial catalyst is already matched.

The ORR data was further analysed by constructing Tafel plots (Figure 3d). The Tafel slope values were found to be about -65 mV at low current densities. This is a typical Tafel slope value for ORR on Pd, which corresponds to the surface covered with oxides (-60 mV) and the reaction is limited by the slow transfer of the first electron to O_2 molecule [32]. At high current densities this value increases to -120 mV as the oxides are reduced, but the rate-limiting step remains the same [32]. Similar Tafel slope values have been reported for various Pd catalysts, including unsupported Pd nanocubes thus showing that the mechanism for the ORR is the same on all of these materials [3, 10, 11, 14, 32].

The results obtained here show that carbon-supported Pd nanocubes are suitable catalysts for oxygen reduction in alkaline solution as they have high specific activity and the mass-activity is close to that of spherical Pd nanoparticles. Thereby cubic Pd nanoparticles can be utilised as cathode catalyst for anion exchange membrane fuel cells.

4. Conclusions

Carbon-supported Pd nanocubes with three different particle sizes were prepared and their electrocatalytic activity towards the ORR was tested in alkaline solution. The TEM analysis showed that the average size of Pd nanocubes was 30, 10 and 7 nm depending on the synthesis method employed. The ORR studies revealed that the specific activity of carbon-supported Pd nanocubes is more than two times higher than that of spherical Pd nanoparticles and commercial Pd/C catalyst. The mass-activities of smallest Pd nanocubes matched that of commercial Pd/C. The RDE analysis showed that the ORR proceeds via 4-electron pathway

and the reaction mechanism is the same on all studied catalysts and is similar to that reported in the literature.

Acknowledgements

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Figure captions

Figure 1. TEM images of carbon-supported Pd nanocubes (a) PdCub1-20, (b) PdCub1-50, (c) PdCub2-20 and (d) PdCub3-20.

Figure 2. (a) Oxidation of pre-adsorbed CO on PdCub3-20, v=20 mV s^{-1}. (b) CVs of carbon-supported Pd nanocubes in Ar-saturated 0.1 M KOH, v=50 mV s^{-1}. Current densities are normalised to the real surface area of electrocatalysts.

Figure 3. (a) A set of RDE results of PdCub3-20 in O_2-saturated 0.1 M KOH and (b) corresponding K-L plots, inset shows the potential dependence of n. (c) Comparison of RDE voltammetry curves for oxygen reduction on Pd/C catalysts in O_2-saturated 0.1 M KOH and (d) corresponding Tafel plots, ω=1900 rpm, v=10 mV s^{-1}. Current densities are normalised to the geometric area of GC.

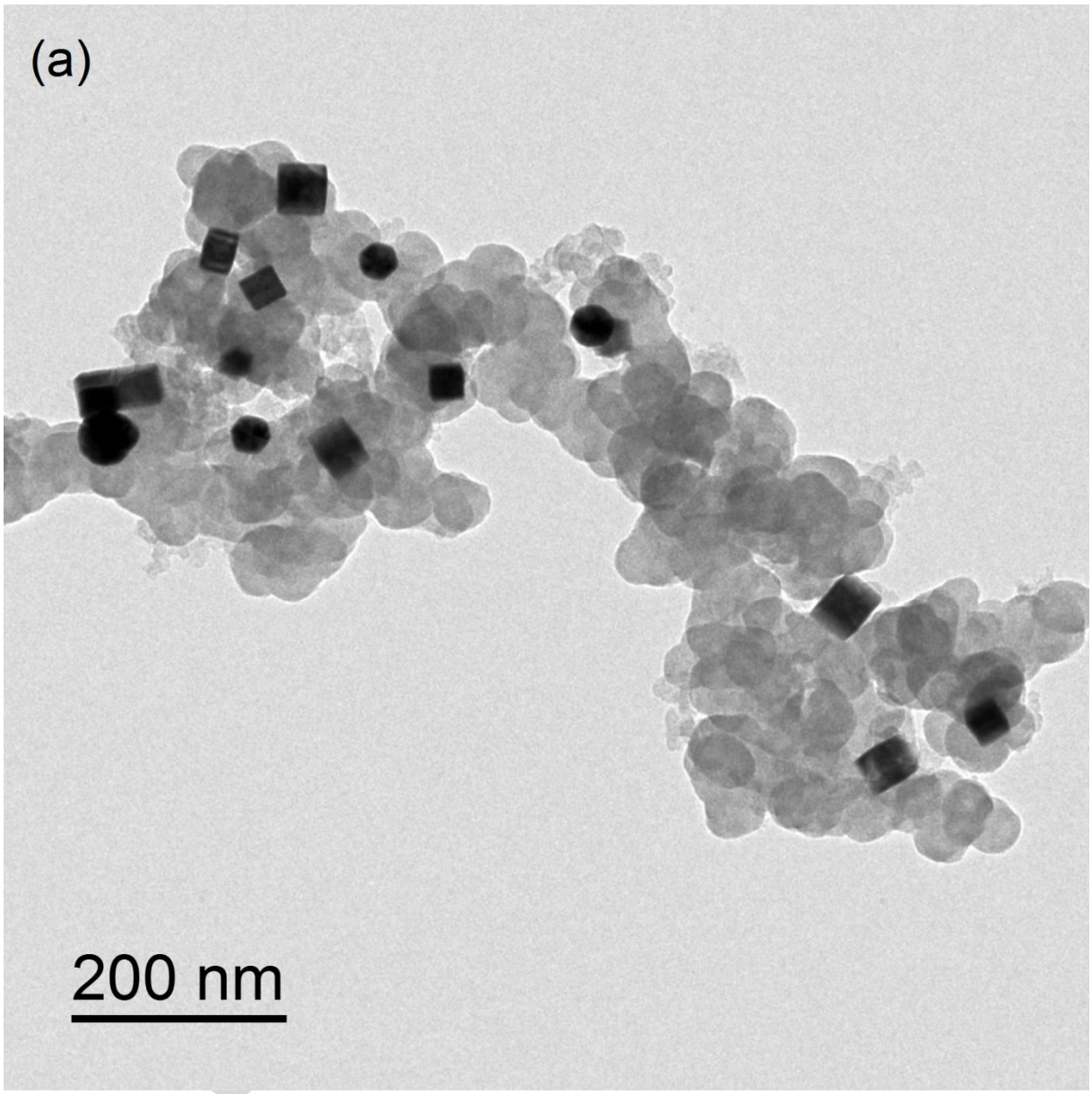


Fig. 1a

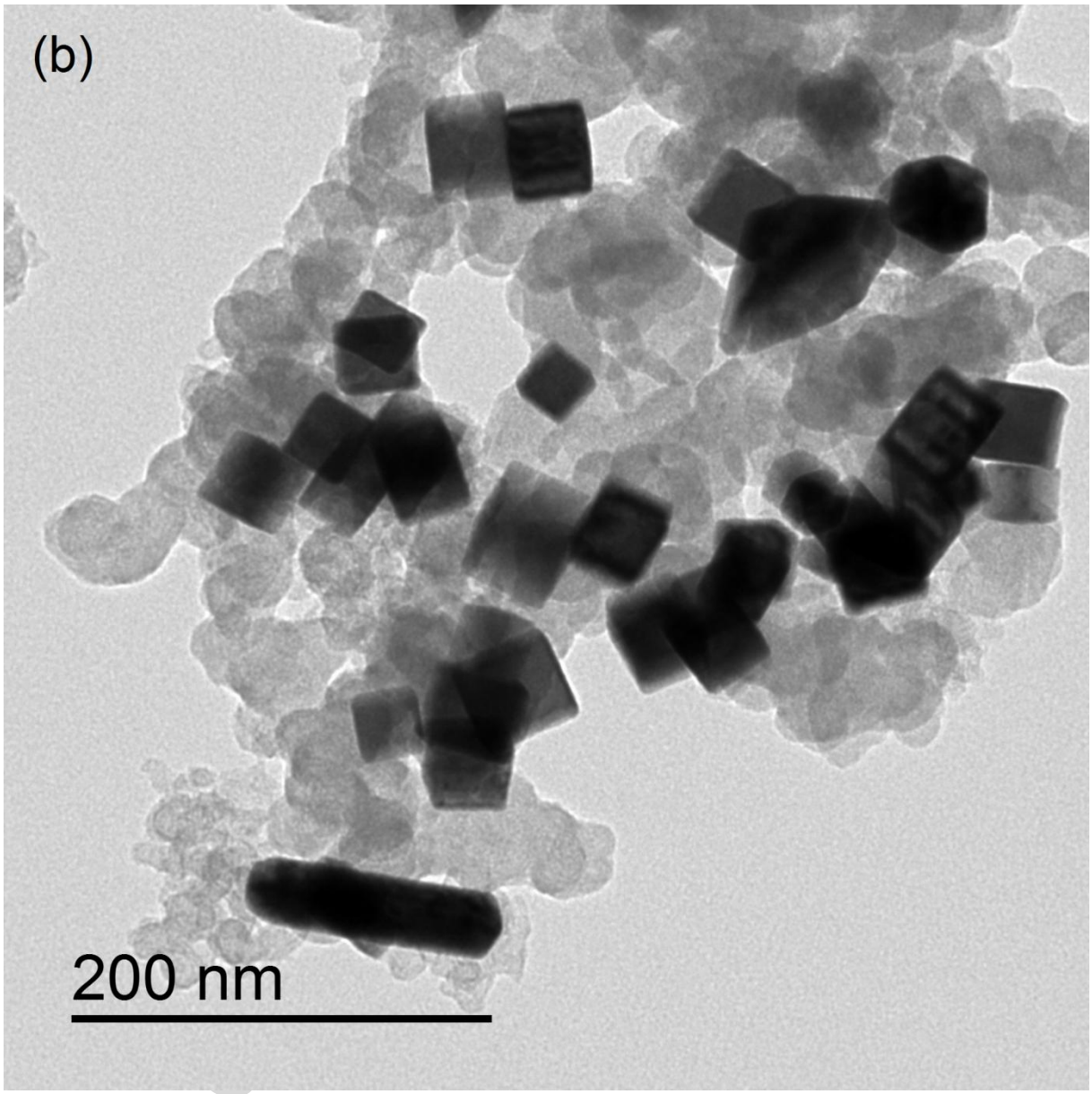


Fig. 1b

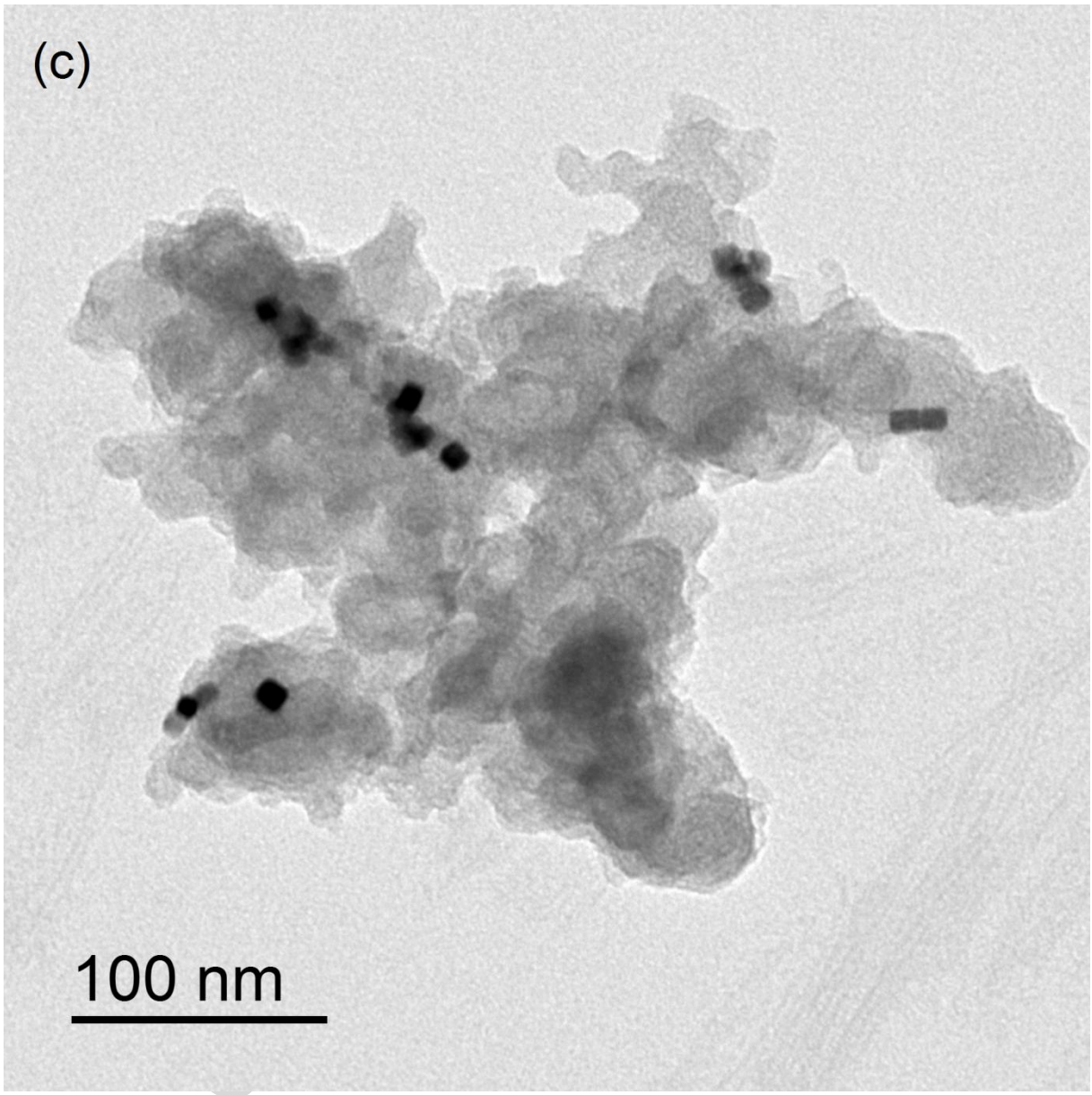
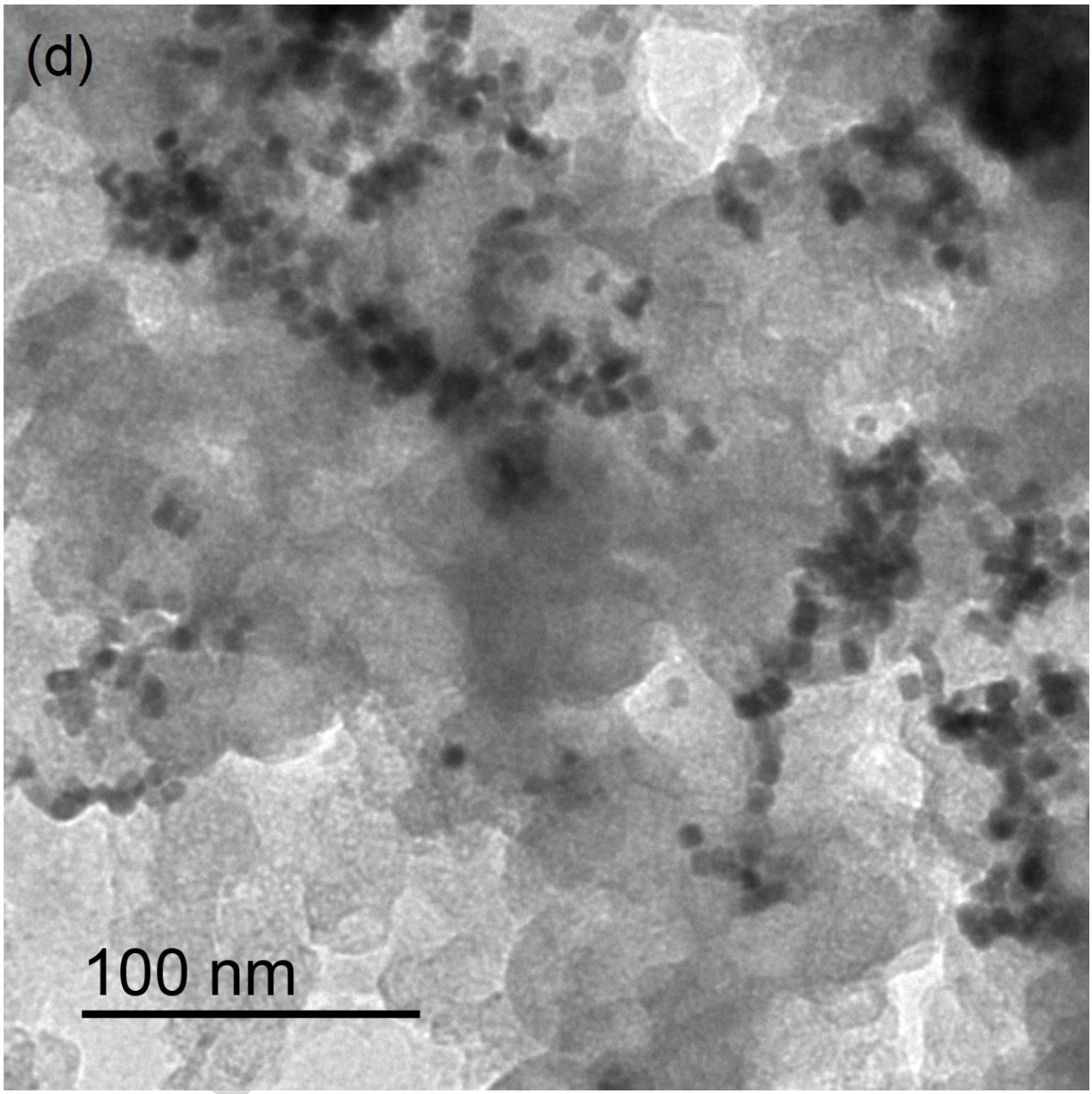


Fig. 1c



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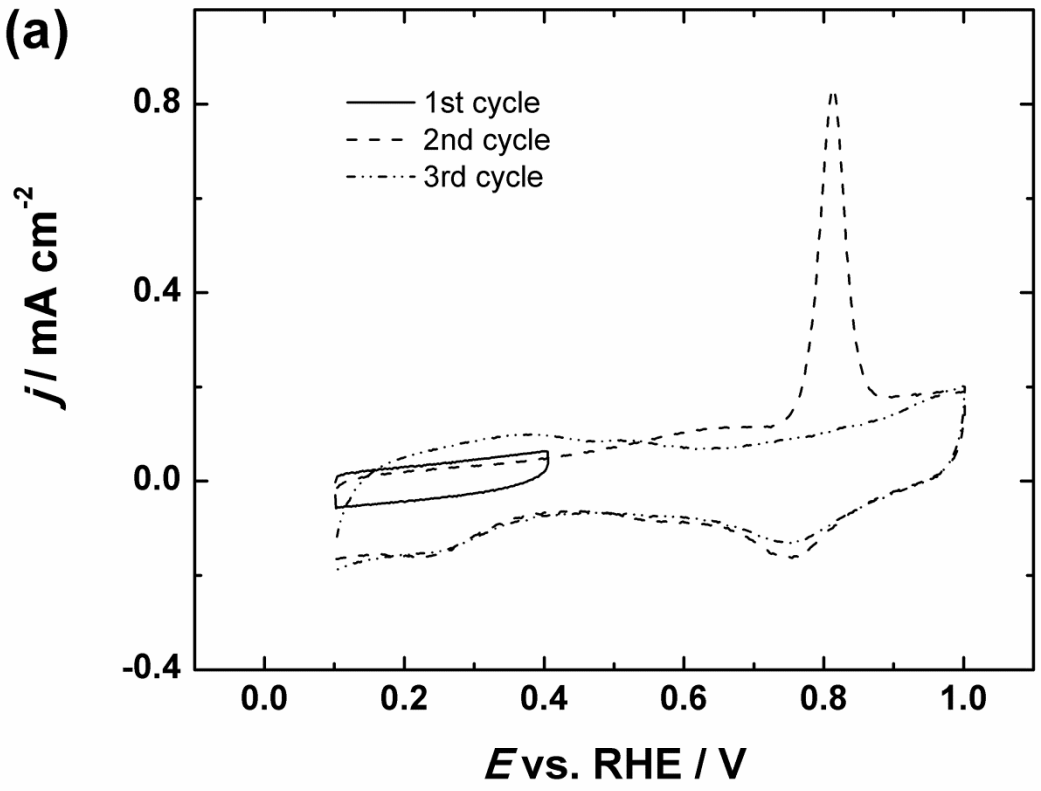
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2nd cycle
3rd cycle
j / mA cm-2
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0.8
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E vs. RHE / V

Fig. 2a

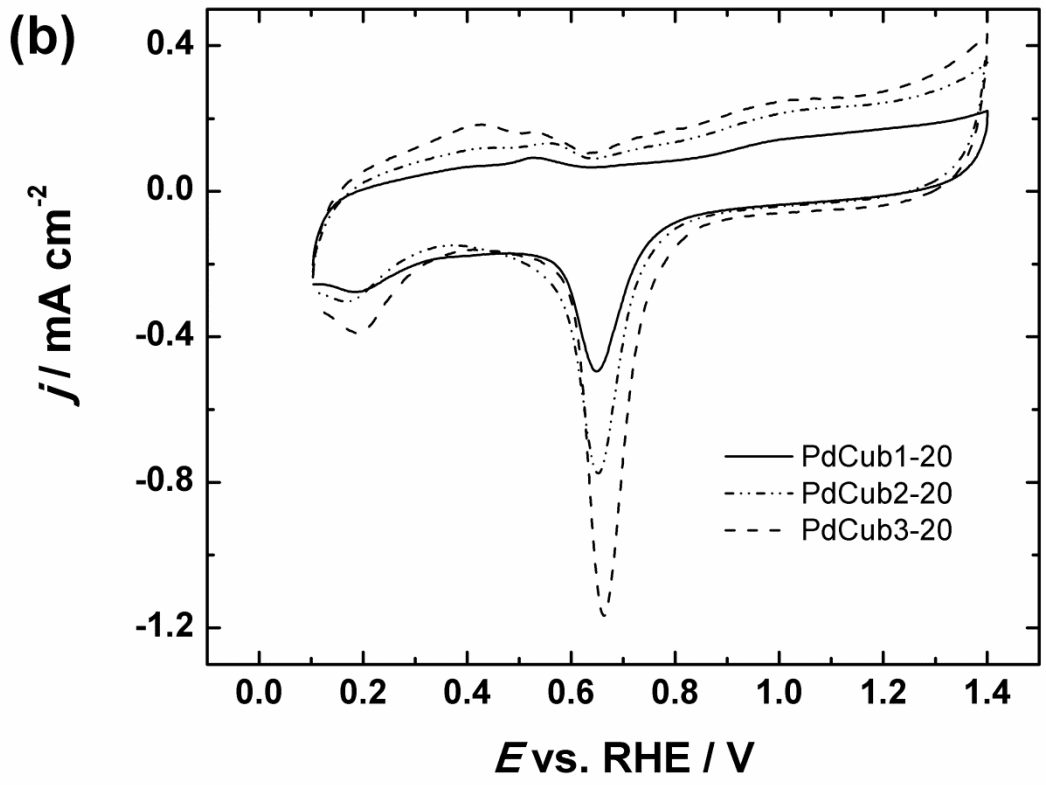


Fig. 2b

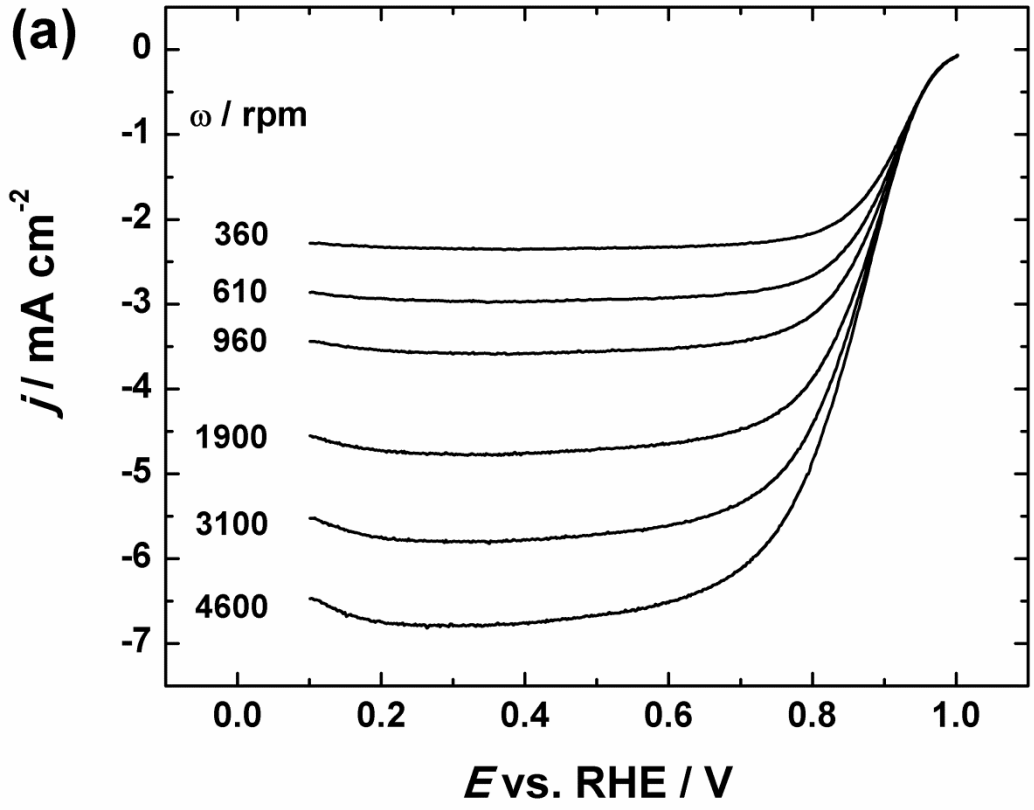


Fig. 3a

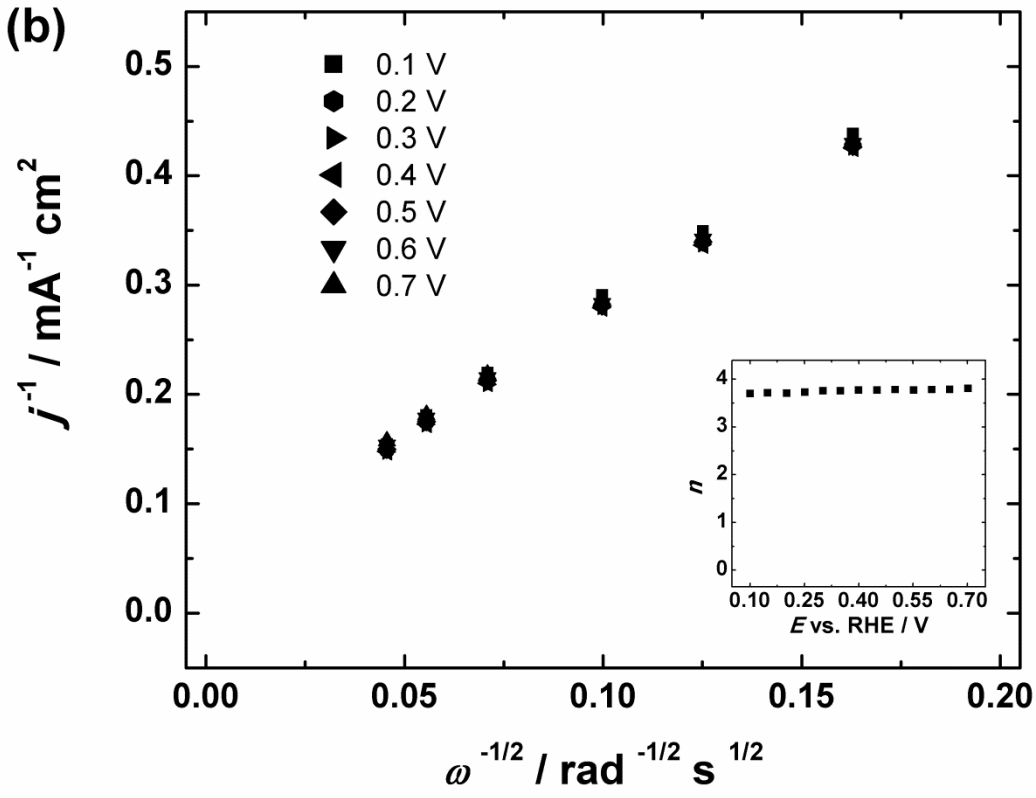
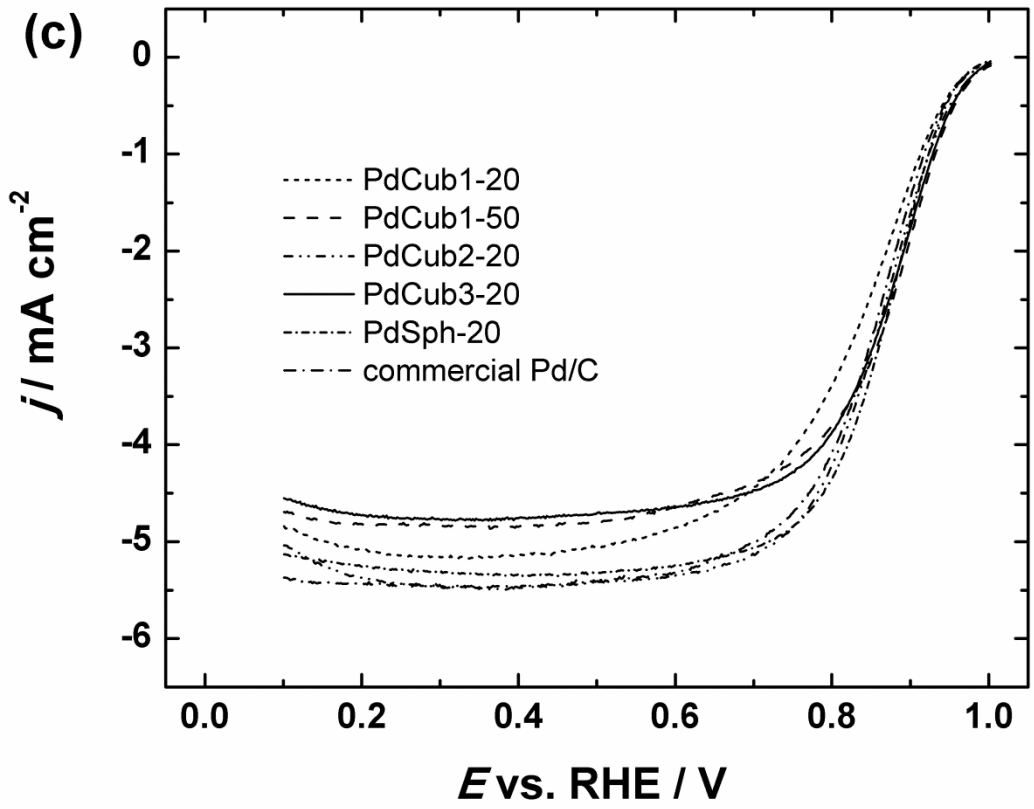


Fig. 3b



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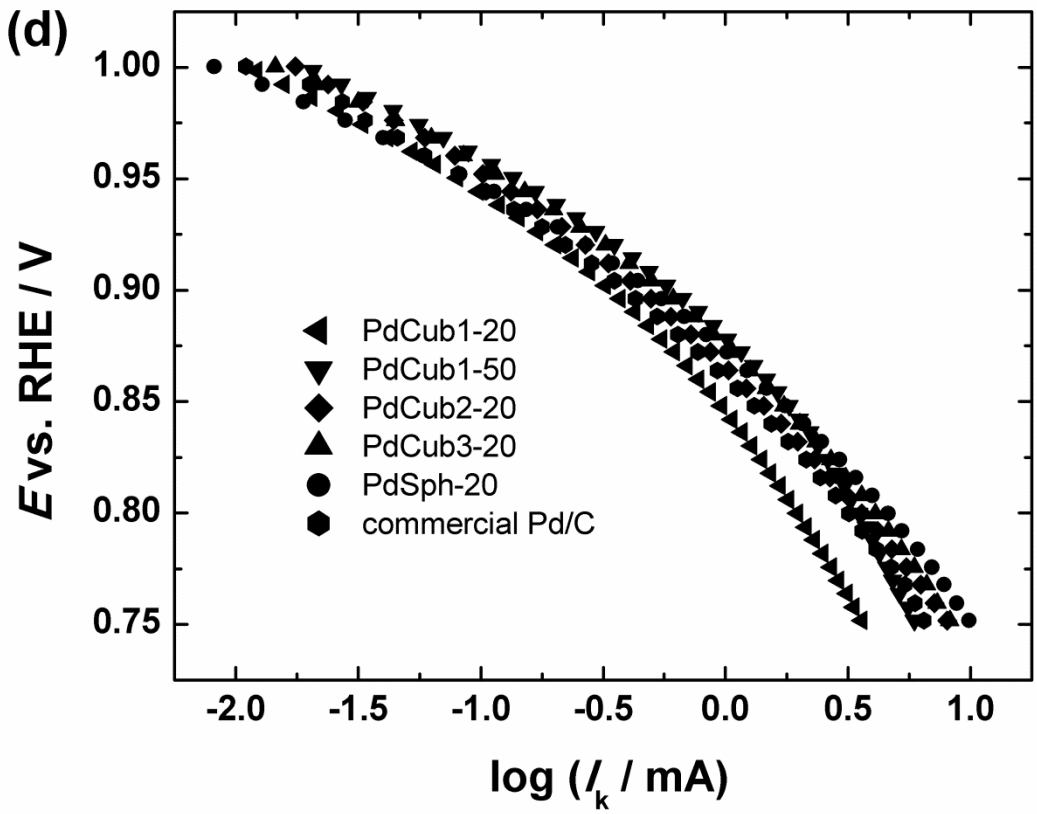
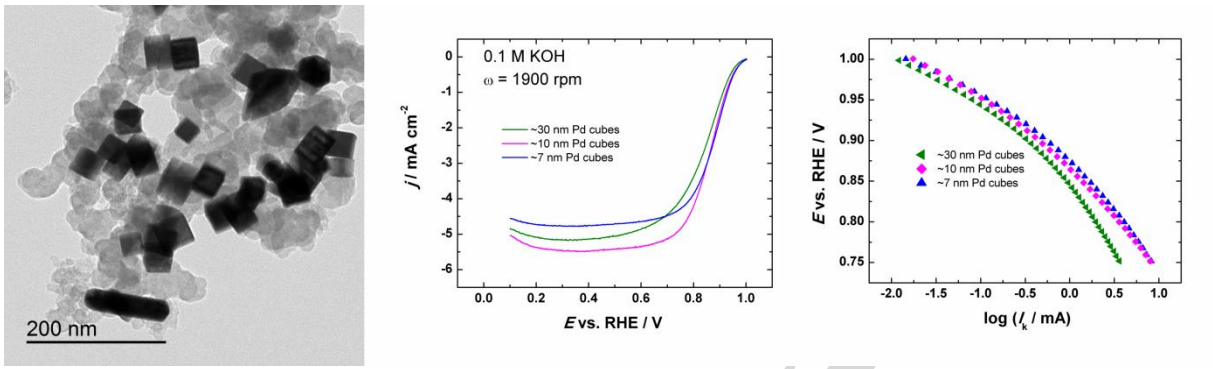


Fig. 3d



Graphical abstract

Research highlights

- Carbon-supported Pd nanocubes of three different size were synthesized
- Specific activity of Pd nanocubes is higher than that of spherical Pd nanoparticles
- The mass-activity of ~7 nm Pd nanocubes matches that of commercial Pd/C
- The oxygen reduction reaction on Pd nanocubes proceeds via 4-electron pathway